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HELIUM ACTIVITY
HELIUM RESEARCH CENTER
INTERNAL REPORT

THERMODYNAMIC CONSISTENCY OF

HELIUM-NITROGEN VAPOR-LIQUID EQUILIBRIA DATA

BY

P. C. Tully

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BRANCH

Branch of Fundamental Research

PROJECT NO.

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HERMODYNAMIC CONSISTENCY OF
HELIUM-NITROGEN VAPOR-LIQUID EQUILIBRIA DATA

by

P. C. Tully^{1/} and J. M. Estes^{2/}

ABSTRACT

The purpose of this investigation was to test the relative consistency of the vapor-liquid equilibria data available in the literature on the helium-nitrogen system. The data of DeVaney, Dalton, and Meeks; Kharakhorin; Buzyna, Macriss, and Ellington; Rodewald, Davis, and Kurata; and Gonikberg and Fastovskii were evaluated by an isothermal consistency test equation recently proposed by Thompson and Edmister. DeVaney's data was the most consistent; Gonikberg's was the least consistent.

INTRODUCTION

As the name implies, thermodynamic consistency tests are performed to determine whether or not one form of experimental data is thermodynamically consistent with another form of experimental data. For isothermal data vapor-liquid equilibria data are usually compared with pressure-volume-temperature data; for isobaric data vapor-liquid equilibria data are usually compared with enthalpy data. Since there are more PVT data than enthalpy data available for the helium-nitrogen system, the isothermal form of the consistency test was selected as a

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basis for comparing the helium-nitrogen vapor-liquid equilibria data available in the literature.

Consistency tests can be performed in either the differential form or the integral form. The former is a point-by-point evaluation of the data, whereas the latter averages all of the data along a given isotherm. The integral form of the test was selected because we wanted to evaluate the data of each investigator in as few segments as possible.

Five sets of data from independent investigators were selected for performing these consistency tests. The pressure and temperature ranges of these data are given in table 1.

TABLE 1. - Helium-nitrogen vapor-liquid equilibria data evaluated

| <u>Source</u> | <u>Pressure range,</u> <u>psia</u> | <u>Temp. range,</u> <u>° K</u> |
|--|---------------------------------------|-----------------------------------|
| DeVaney, Dalton, and Meeks (4) ^{3/} | 200-2000 | 77.0-120.0 |
| Kharakhorin (7) | 66-3152 | 68.0-111.5 |
| Buzyna, Macriss, and Ellington (2) | 169-1001 | 77.2-122.8 |
| Rodewald, Davis, and Kurata (12) | 200-1000 | 64.9- 77.2 |
| Gonikberg and Fastovskii (6) | 263-4196 | 78.0-109.0 |

^{3/} Underlined numbers in parentheses refer to items in the list of references at the end of this report.

The investigations of Fedoritenko and Ruhemann (5), as well as those of several other authors, have not been included in this group of consistency tests because they did not publish numerical data.

An IBM 1620 digital computer was used extensively in carrying out the calculations required for this report.

ISOTHERMAL INTEGRAL CONSISTENCY TEST EQUATION AND ITS EVALUATION

The consistency test equation utilized in this internal report to evaluate the helium-nitrogen vapor-liquid equilibria data is one recently proposed by Thompson and Edmister (14), which is

$$\int_{\ln K_1, P_1}^{\ln K_1, P_2} x_1(1 + y_1 \xi_1) d \ln K_1 + \int_{\ln K_2, P_1}^{\ln K_2, P_2} x_2(1 + y_1 \xi_1) d \ln K_2 = \int_{P_1}^{P_2} \frac{V^L - x_1 \bar{V}_1^V - x_2 \bar{V}_2^V}{RT} dP \quad (1)$$

where

$$\xi_1 = \frac{1}{RT} \int_0^P \left(\frac{\partial \bar{V}_1}{\partial y_1} \right)_{P,T} dP \quad (2)$$

A complete derivation of equation (1) is given in Appendix I. For a vapor which obeys the Lewis and Randall fugacity rule, $\xi_1 = 0$, and equation (1) reduces to the equation of Adler, et al. (1).

In order to test the consistency of the data, it is necessary to compare the summation of the terms on the left-hand side of the equation with the term on the right-hand side. The better the agreement is between the opposing sides of the equation, the more consistent the data.

The quantities x_1 , y_1 , K_1 , x_2 , y_2 , K_2 , T , and P were taken directly from the data. A list of the notation used in this report is appended.

The ξ_1 term was evaluated using an equation of Thompson which was derived from the Berlin-form virial equation of state. His derivation

is given in Appendix II. While the original derivation includes the second and third virial coefficients, only the second coefficients were used to evaluate ξ_1 in this report. Thompson (15) says this omission does not significantly affect the results. The virial coefficients used were calculated using an equation of Wood, et al. (16).

In the absence of complete PVT data in the two-phase region, the volumetric terms on the right-hand side of the equation were calculated from various equations of state. V_{Mix}^L (for the mixture) was assumed to be equal to V_2^L (for pure nitrogen), and the latter calculated by an equation given by Strohbridge (13). V_{Mix}^V and \bar{V}_1^V were calculated by the Redlich-Kwong (10) equation of state, and a partial molal volume equation given by Prausnitz (9), respectively. \bar{V}_2^V was calculated from the partial molal volume equation

$$V^V = y_1 \bar{V}_1^V + y_2 \bar{V}_2^V \quad (3)$$

Use of these equations is covered in detail in Appendix III.

Rodewald, Davis, and Kurata (12) published values for the densities of the coexisting phases at 64.9, 69.3, and 77.2° K, which were obtained by using a system of simultaneous equations. These densities were inverted to obtain the molal volume terms which were used to evaluate their data. The partial molal volume term was obtained from the Prausnitz (9) equation, which is based on the Redlich-Kwong equation.

The integration of the first term on the left-hand side of equation (1) was carried out by evaluating $x_1(1 + y_1\xi_1)$ and $\ln K_1$

at each pressure along a given isotherm for a particular investigation. Least-squares regressions were then made on these data using the $x_1(1 + y_1\xi_1)$ term as ordinate, and the $\ln K_1$ term as abscissa, and second, third, fourth, and fifth degree polynomials as models. Each of the resulting equations, which expressed $x_1(1 + y_1\xi_1)$ as a function of $\ln K_1$, was integrated between the limits of $\ln K_1$ evaluated at the lowest pressure and $\ln K_1$ evaluated at the highest pressure. The values of these integrals were used to select the polynomial which represented the data best. When the integrals of two consecutive polynomials agreed to within 2 1/2 percent, we selected the lower order polynomial for use in the consistency test.

To illustrate this procedure, let us examine the polynomials of the first integral, A_1 , for DeVaney's 77.0° isotherm. The values for the first integral on the left-hand side are tabulated below:

| Degree of Polynomial | A_1 |
|----------------------|--------|
| Second | .01637 |
| Third | .01659 |
| Fourth | .01657 |

The second order equation was selected as the one which best represented the data for this isotherm. This produced an equation of the form

$$x_1(1 + y_1\xi_1) = A + B \ln K_1 + C(\ln K_1)^2 \quad (4)$$

where A, B, and C are the constants determined by the least squares regression.

The second term on the left-hand side was treated in much the same manner as the first term. The right-hand side of the equation, however, could not be fitted with an equation of that form. Therefore, an equation of the form

$$\underline{V}^L - x_1 \bar{V}_1^V - x_2 \bar{V}_2^V = A + \frac{B}{P} + \frac{C}{P^2} \quad (5)$$

was used.

Typical curves for the three equations are shown in figure 2. The integration was carried out from the lowest pressure, point 1, to the highest pressure, point 2. Some investigators added the vapor-pressure data of pure nitrogen to their vapor-liquid equilibria data to test the consistency of their data using other consistency test equations. This technique was attempted in the preparation of this report. While the effect on the terms on the left-hand side was acceptable, the effect of adding this point to the right-hand term was not. From figure 1, it can be seen that the contribution made by the pure nitrogen point to the area under the curve is very sizeable.

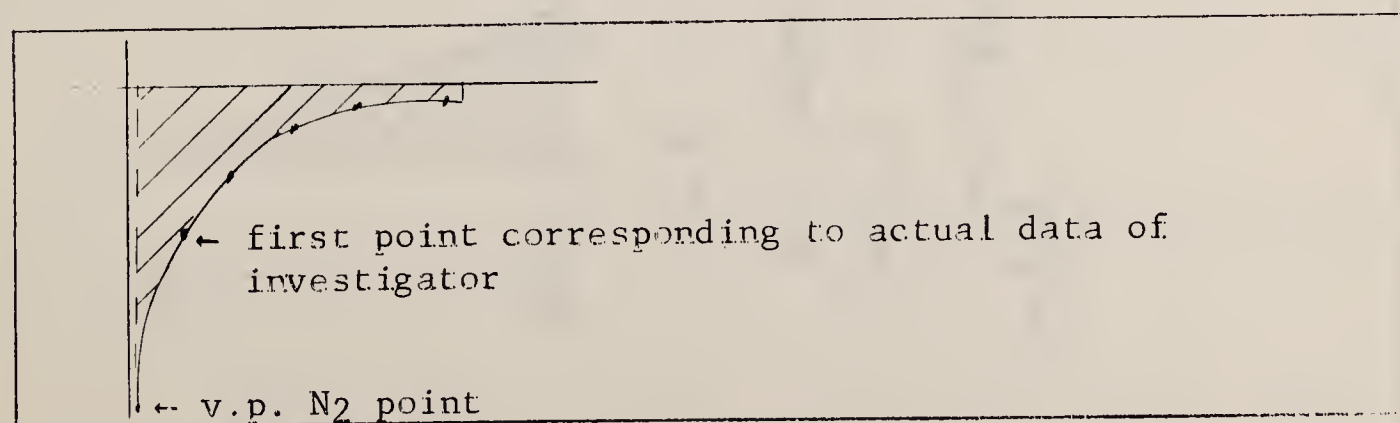


Figure 1. - Effect of pure N_2 point on A_3

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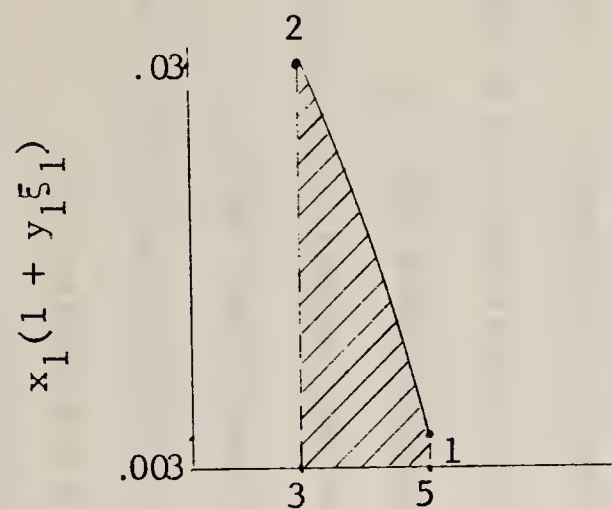
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$$E = \frac{1}{2}mv^2 + \frac{1}{2}I\omega^2$$

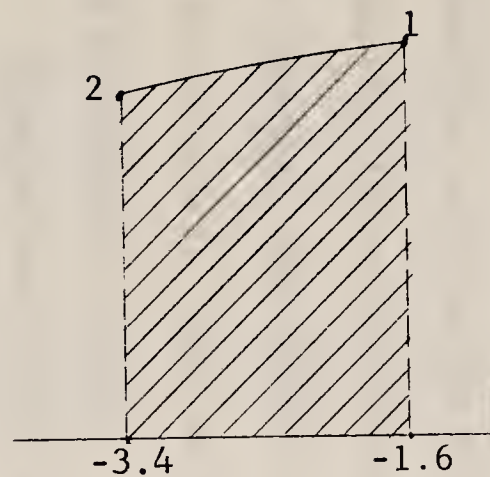
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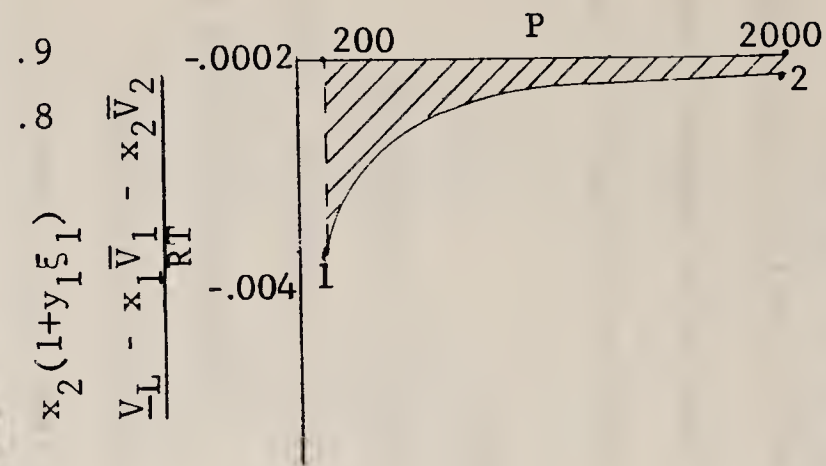
Figure 1: A graph of the function $y = f(x)$ showing its increasing and concave-down nature.



$$A_1 = -.02490 = \int_{\ln K_1, P_1}^{\ln K_1, P_2} x_1(1+y_1\xi_1) d \ln K_1$$



$$A_2 = -1.47 = \int_{\ln K_2, P_1}^{\ln K_2, P_2} x_2(1+y_1\xi_1) d \ln K_2$$



$$A_3 = -1.48 = \int_{P_1}^{P_2} \left(\frac{V^L - x_1 V_1^V - x_2 V_2^V}{RT} \right) dP$$

Figure 2. - Typical integrals

Furthermore, the shape of the curve between the two points has a significant effect on the value of A_3 . Therefore, the use of the pure nitrogen data point was deleted from all terms to eliminate the introduction of this uncertainty.

DISCUSSION OF RESULTS

The results of the consistency test are given in table 2 and plotted in figure 3. The investigators have been ranked in order of their consistency.

Recalling that each area could be in error by as much as 2 1/2 percent, the most probable error in the answer would be 4.3%. Therefore, any results within $\pm 4.3\%$ are considered consistent. Likewise, if any two investigators' results are within 4.3% of one another, they have to be considered as being of the same order of consistency. This is illustrated in the case of DeVaney (4.6%) and Kharakhorin (7.0%).

Examination of the results in detail indicates that the high temperature results of each investigator are less consistent than the low temperature results. Virtually none of the data above 110° K is consistent at all. Four possible reasons for this are:

1. The Redlich-Kwong equation does not predict the compressibility of nitrogen-rich vapor too well.
2. The liquid sampling methods of most investigators were such that fractionation may have occurred.
3. The values for ξ_1 may be more in error at the higher nitrogen concentrations associated with the higher temperatures.

TABLE 2. - Results of consistency test^{1/}

| T, ° K | P range, psia | A ₁ | A ₂ | A ₁ +A ₂ | A ₃ | $\frac{\text{Diff.}}{A_3} \left(\frac{A_3 - (A_1 + A_2)}{A_3} \right) (100\%)$ | % Diff. |
|--------------------------|------------------|----------------|----------------|--------------------------------|----------------|---|-----------------|
| DeVaney, et al. | | | | | | | |
| 77.0 | 200→2000 | -.0164 | -1.65 | -1.67 | -1.54 | .13 | -8.5 |
| 80.0 | 200→2000 | -.0196 | -1.66 | -1.68 | -1.52 | .16 | -10.3 |
| 85.0 | 200→2000 | -.0249 | -1.47 | -1.49 | -1.48 | .01 | -.7 |
| 90.0 | 200→2000 | -.0292 | -1.37 | -1.40 | -1.41 | -.01 | .9 |
| 95.0 | 200→2000 | -.0309 | -1.28 | -1.31 | -1.32 | -.009 | .7 |
| 100.0 | 200→2000 | -.0320 | -1.16 | -1.19 | -1.22 | -.03 | 2.1 |
| 105.0 | 200→2000 | -.0300 | -1.00 | -1.03 | -1.09 | -.06 | 5.9 |
| 110.0 | 400→2000 | -.0240 | -.482 | -.506 | -.554 | -.048 | 8.6 |
| 115.0 | 400→2000 | -.0142 | -.334 | -.348 | -.412 | -.064 | 15.6 |
| 120.0 | 600→2000 | -.0061 | -.100 | -.106 | -.155 | -.049 | 31.9 |
| | | | | | | avr. = | 4.6 ± 12.2 |
| Kharakhorin | | | | | | | |
| 68.0 | 66→2124 | -0.0122 | -2.59 | -2.60 | -2.46 | 0.14 | -5.6 |
| 77.3 | 71→2329 | -.0234 | -2.51 | -2.53 | -2.54 | -.01 | 0.5 |
| 90.1 | 71→3152 | -.0431 | -2.54 | -2.58 | -2.40 | .18 | -7.9 |
| 107.0 | 514→2219 | -.0200 | -.338 | -.358 | -.465 | -.107 | 22.9 |
| 111.5 | 285→2866 | -.0178 | -.487 | -.505 | -.674 | -.169 | 25.1 |
| | | | | | | avr. = | 7.0 ± 15.8 |
| Buzyna, et al. | | | | | | | |
| 77.2 | 169→1001 | -.0095 | -1.32 | -1.33 | -1.31 | -.02 | -1.4 |
| 92.9 | 169→998 | -.0183 | -1.04 | -1.06 | -1.17 | -.11 | 9.6 |
| 112.1 | 499→998 | -.0093 | -.190 | -.199 | -.239 | -.040 | 16.4 |
| 118.1 | 499→998 | -.0092 | -.158 | -.167 | -.153 | .014 | -9.6 |
| 122.8 | 499→998 | -.0106 | -.132 | -.143 | -.082 | .061 | -73.5 |
| | | | | | | avr. = | 10.7 ± 24.7 |
| Rodewald, et al. | | | | | | | |
| 64.9 | 200→1000 | -.0050 | -.978 | -.983 | -1.09 | -.11 | 10.3 |
| 69.3 | 200→1000 | -.0066 | -.750 | -.757 | -1.16 | -.40 | 34.6 |
| 77.2 | 200→1000 | -.0093 | -1.20 | -1.21 | -1.15 | .06 | -5.0 |
| | | | | | | avr. = | 13.3 ± 19.9 |
| Gonikberg and Fastovskii | | | | | | | |
| 78.0 | 263→4196 | -.0326 | -1.22 | -1.25 | -1.43 | -.18 | 12.5 |
| 90.1 | 294→4053 | -.0384 | -.949 | -.987 | -1.19 | -.20 | 17.0 |
| 109.0 | 391→4068 | .0051 | -.170 | -.165 | -.554 | -.389 | 70.2 |
| | | | | | | avr. = | 33.2 ± 32.1 |

^{1/} Rounded from standard eight-digit precision.

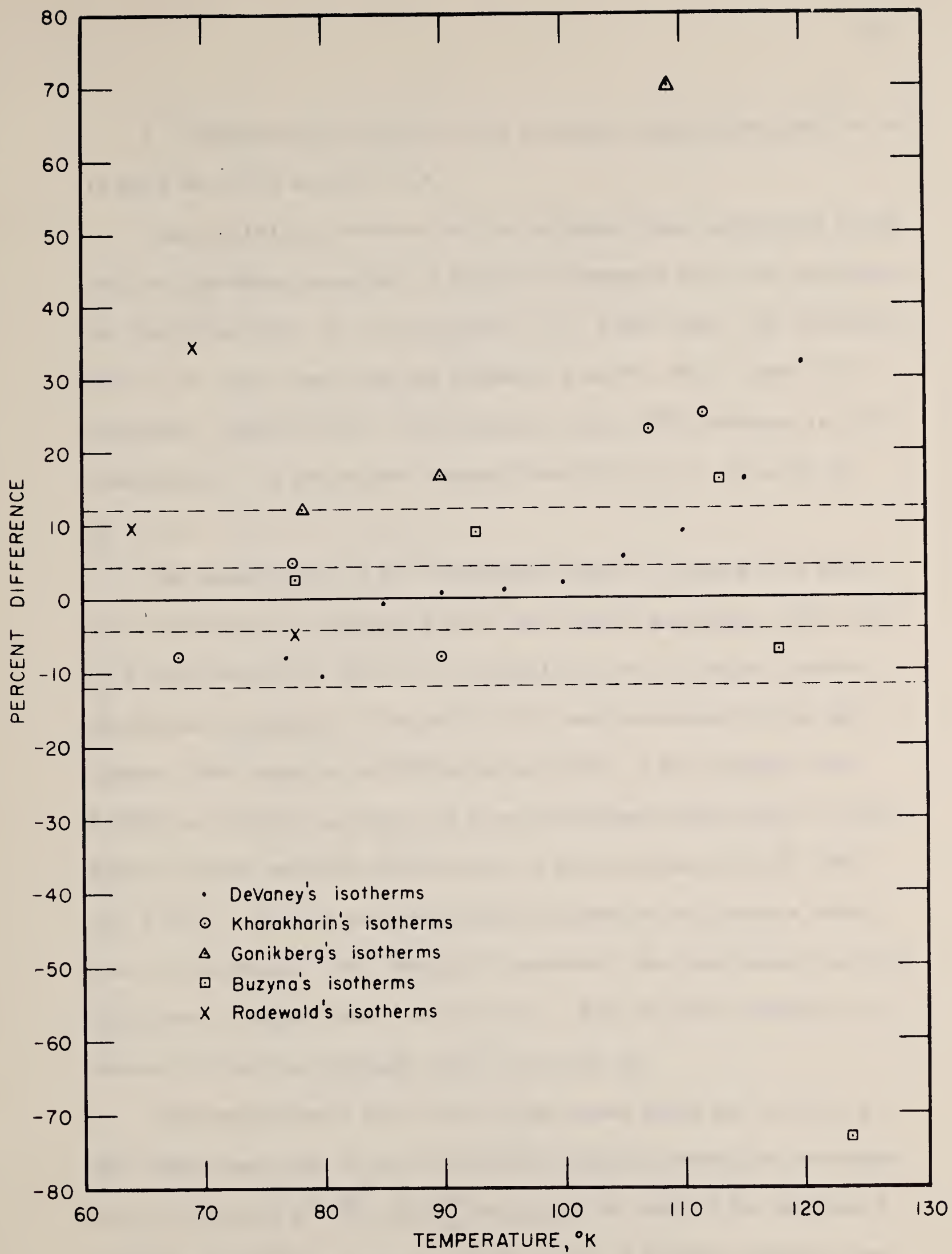


FIGURE 3.—Percent Difference In Consistency Test

4. Temperature control at the elevated temperatures may not be as good as it is around 77° K.

Compressibility factors for the mixtures were calculated using the Redlich-Kwong equation of state and compared with the experimental data available in the literature. At 1,000 psia, the deviations were 4.1%, 3.1%, and 3.4% for Rodewald's 64.9°, 69.3°, and 77.2° isotherms, respectively. For Canfield's (3) 133° isotherm at 250 atmospheres, the deviations ranged from 2% at $y_1 = .15$ to 7% at $y_1 = 1.0$.

The sensitivity of the consistency test to errors in x and y was determined for DeVaney's 85.0° and 120.0° isotherms. The value of x was reduced by 10% of the composition or 0.01 mole fraction, whichever was smaller. The value of y was increased by the same amount. For example, at 200 psia and 85.0°, x was changed from 0.0039 to 0.0035; the value of y was increased from 0.806 to 0.816. These changes produced an increase in the K-value of 12.8% (206.7 vs. 233.1). Similar perturbations were made at all points along the two isotherms. For the 85.0° isotherm, the consistency percent difference changed from -.7 to -18.7. For the 120° isotherm, the percent difference changed from 31.9 to 27.2.

The magnitudes of the three volume terms which go to make up the right-hand side of the consistency equation were also investigated. Values of \underline{V}^L , \overline{V}_1^V , and \overline{V}_2^V are given in table 3 for DeVaney's 77.0° and 120.0° isotherms at the lowest and highest pressure run on each isotherm. Examination of the penultimate column indicates

TABLE 3. - Magnitude of terms on right side for DeVaney's 77° and 120° isotherms

| T, ° K | P, psia | x ₁ | \bar{V}_1^V | x ₂ | \bar{V}_2^V | \underline{V}^L | $-(x_1)(\bar{V}_1)^V$ | $-(x_2)(\bar{V}_2)^V$ | $\frac{\underline{V}^L - (x_1)(\bar{V}_1)^V - (x_2)(\bar{V}_2)^V}{RT}$ |
|-----------|------------|----------------|---------------|----------------|---------------|-------------------|-----------------------|-----------------------|--|
| 77 | 200 | .0026 | 481 | .997 | 419 | 34.6 | -1.25 | -418 | -384 |
| 77 | 2000 | .0214 | 62.2 | .979 | 54.0 | 34.6 | -1.33 | -52.8 | -19.5 |
| 120 | 600 | .0253 | 427 | .975 | 97.5 | 53.1 | -10.8 | -95.0 | -52.7 |
| 120 | 2000 | .140 | 98.9 | .860 | 46.0 | 53.1 | -13.8 | -39.6 | -.3 |

| | |
|------|----|
| 1115 | 43 |
| 1116 | 55 |
| 1117 | 6 |
| 1118 | 44 |
| 1119 | 4 |
| 1120 | 4 |
| 1121 | |
| 1122 | 4 |
| 1123 | 5 |
| 1124 | 4 |
| 1125 | 4 |

that the value of the right-hand side of the equation is largely attributable to the low pressure data. This minimized the effect of the error induced by assuming that the liquid is pure nitrogen. The magnitude of \bar{V}_2^V is seen to be important at all points. Thus, the consistency test is dependent on the ability of the Redlich-Kwong equation to predict the compressibility of the vapor.

CONSISTENCY TEST USED BY BUZYNA AND RODEWALD

Both Buzyna (2) and Rodewald (12) used Adler's consistency test on their data. Neither of these investigators incorporated the ξ_1 term to account for the nonideality of the vapor. Both used graphical integration which is less accurate than the digital computer methods utilized in this report. Both used the vapor pressure of nitrogen as the lower limit of integration, which we did not.

Both of these investigators made simplifying assumptions to carry out their consistency tests. Buzyna made the assumption that $\bar{V}_1^V = \underline{V}_1^V$. He used four combinations of sources of volumetric data and got widely differing answers by these four methods. Two of the sources involved the use of generalized charts. The other two were Otto's (8) equation for helium compressibility factors and experimental data for Z_2^L . Even when he used Otto's equation for Z_1 , he still used generalized charts to compute Z_m .

Rodewald used his own volumetric data, of course. He assumed that $Z_1^V = Z_m^V$. Thus, he was able to simplify

$$\left[Z_m^L + Z_1^V y_1 \left(\frac{1}{K_2} - \frac{1}{K_1} \right) - \frac{Z_m^V}{K_2} \right] \text{ to } \left[Z_m^L - Z_m^V \right]. \text{ At the low temperatures}$$

where his data were taken (64° to 77°), this is not as serious an error as it is at 120° (y_2 increases with temperature).

There is qualitative agreement between the consistency test results of these two investigators, and the results of this report.

CONCLUSIONS

Before the results of this work can be made conclusive, it will be necessary to correct some of the deficiencies indicated above in the prediction of thermodynamic properties. Other consistency tests can also be performed. This work is currently underway.

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APPENDIX I

DERIVATION OF THOMPSON-EDMISTER EQUATION

This test is based on the following general form of the Gibbs-Duhem equation

$$\sum n_i d\mu_i = -SdT + VdP$$

This equation can be derived as follows.

Consider first a reversible process acting on a closed system wherein fluid pressure is the only acting force, then by the First and Second Laws of Thermodynamics

$$H = U + PV \quad (I-1)$$

$$dH = dU + PdV + VdP \quad (I-2)$$

$$U = TdS - PdV \quad (I-3)$$

Substituting the value of dU from equation (I-3) into equation (I-2) gives

$$dH = TdS + VdP \quad (I-4)$$

The Gibbs free energy function G is defined by

$$G = H - TS \quad (I-5)$$

from which

$$dG = dH - TdS - SdT \quad (I-6)$$

Substituting the value of dH from equation (I-4) into equation (I-6)

$$dG = VdP - SdT \quad (I-7)$$

In order to introduce μ_i , where

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T} \quad (I-8)$$

now consider an open (variable mass) system, where

$$G = G(T, P, n_1, \dots, n_n) \quad (I-9)$$

General differentiation gives

$$dG = \left(\frac{\partial G}{\partial T} \right)_{P, n_i} dT + \left(\frac{\partial G}{\partial P} \right)_{T, n_i} dP + \sum_{i=1}^n \left(\frac{\partial G}{\partial n_i} \right)_{T,P} dn_i \quad (I-10)$$

From equation (I-7)

$$\left(\frac{\partial G}{\partial P} \right)_{T, n_i} = V \quad (I-11)$$

$$\left(\frac{\partial G}{\partial T} \right)_{P, n_i} = -S \quad (I-12)$$

Substituting these values in equation (I-10)

$$dG = -SdT + VdP + \sum \left(\frac{\partial G}{\partial n_i} \right)_{T,P} dn_i \quad (I-13)$$

Specifying conditions of constant P and T , and integrating gives

$$G = \sum \mu_i n_i \quad (I-14)$$

(See equation (I-8) for μ_i .)

General differentiation of equation (I-14) gives

$$dG = \sum \mu_i dn_i + \sum n_i d\mu_i \quad (I-15)$$

(At conditions of constant P and T, $\sum n_i d\mu_i = 0$.)

Comparing equations (I-13) and (I-15)

$$\sum n_i d\mu_i = -SdT + VdP \quad (I-16)$$

This completes the derivation of the Gibbs-Duhem equation.

Equation (I-16) will now be written for a closed system in equilibrium. Dividing equation (I-16) by the total number of moles, $\sum n_i$ where

$$x_i = n_i / \sum n_i$$

$$\sum x_i d\mu_i = -\underline{S}dT + \underline{V}dP \quad (I-17)$$

where \underline{S} is molal entropy and \underline{V} is molal volume. Since

$$\mu_i = \mu_i(P, T, x_i)$$

$$d\mu_i = \left(\frac{\partial \mu_i}{\partial P} \right)_{T, x_i} dP + \left(\frac{\partial \mu_i}{\partial T} \right)_{P, x_i} dT + \left(\frac{\partial \mu_i}{\partial x_i} \right)_{T, P} dx_i \quad (I-18)$$

From equation (I-11)

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T, x_i} = \left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial n_i} \right)_{P, T} \right]_{T, x_i} = \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P} \right)_{T, x_i} \right]_{P, T} = \left(\frac{\partial \underline{V}_i}{\partial n_i} \right)_{P, T} = \bar{V}_i \quad (I-35)$$

Similarly, from equation (I-12)

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P, x_i} = -S$$

Substituting in equation (I-18) gives

$$d\mu_i = \bar{V}_i dP - \bar{S}_i dT + \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T, P} dx_i \quad (I-19)$$

Combining equations (I-17) and (I-19) at constant P and T,

$$\sum x_i \left(\frac{\partial \mu_i}{\partial x_i}\right)_{P, T} dx_i = 0 \quad (I-20)$$

Equations (I-19) and (I-20) can be written separately for liquid and gas phases, or

$$d\mu_i^L = \bar{V}_i^L dP - \bar{S}_i^L dT + \left(\frac{\partial \mu_i^L}{\partial x_i}\right)_{P, T} dx_i \quad (I-21a)$$

$$d\mu_i^V = \bar{V}_i^V dP - \bar{S}_i^V dT + \left(\frac{\partial \mu_i^V}{\partial y_i}\right)_{P, T} dy_i \quad (I-21b)$$

$$\sum x_i \left(\frac{\partial \mu_i^L}{\partial x_i}\right)_{P, T} dx_i = 0 \quad (I-22a)$$

$$\sum y_i \left(\frac{\partial \mu_i^V}{\partial y_i}\right)_{P, T} dy_i = 0 \quad (I-22b)$$

If the phases coexist in equilibrium, an additional condition is imposed which is

$$d\mu_i^L = d\mu_i^V \quad (I-23)$$

Substituting equations (I-21a) and (I-21b) into equation (I-23) and rearranging

$$\left(\frac{\partial \mu_i^L}{\partial x_i}\right)_{P,T} dx_i - \left(\frac{\partial \mu_i^V}{\partial y_i}\right)_{P,T} dy_i = (\bar{V}_i^V - \bar{V}_i^L) dP - (\bar{S}_i^V - \bar{S}_i^L) dT \quad (I-24)$$

$$= \Delta \bar{V}_i dP - \Delta \bar{S}_i dT \quad (I-25)$$

where $\Delta \bar{S}_i$ = partial molal entropy difference between equilibrium vapor and liquid.

Every term in equation (I-25) is multiplied by x_i . The resulting equation is expanded for a binary system

$$\left[\begin{aligned} & x_1 \left(\frac{\partial \mu_1^L}{\partial x_1}\right)_{P,T} dx_1 + x_2 \left(\frac{\partial \mu_2^L}{\partial x_2}\right)_{P,T} dx_2 \\ & - x_1 \left(\frac{\partial \mu_1^V}{\partial y_1}\right)_{P,T} dy_1 - x_2 \left(\frac{\partial \mu_2^V}{\partial y_2}\right)_{P,T} dy_2 \end{aligned} \right] = (x_1 \Delta \bar{V}_1 + x_2 \Delta \bar{V}_2) dP - (x_1 \Delta \bar{S}_1 + x_2 \Delta \bar{S}_2) dT \quad (I-26)$$

so that equation (I-26) describes the liquid phase of a binary system.

Expanding equation (I-22a) for a liquid phase,

$$x_1 \left(\frac{\partial \mu_1^L}{\partial x_1}\right)_{P,T} dx_1 + x_2 \left(\frac{\partial \mu_2^L}{\partial x_2}\right)_{P,T} dx_2 = 0 \quad (I-27)$$

and (I-22b) for the vapor phase

$$y_1 \left(\frac{\partial \mu_1^V}{\partial y_1}\right)_{P,T} dy_1 + y_2 \left(\frac{\partial \mu_2^V}{\partial y_2}\right)_{P,T} dy_2 = 0 \quad (I-28)$$

Rearranging and recalling that $dy_1 = -dy_2$

$$\left(\frac{\partial \mu_2^V}{\partial y_2}\right)_{P,T} = \frac{y_1}{y_2} \left(\frac{\partial \mu_1^V}{\partial y_1}\right)_{P,T} \quad (I-29)$$

Substituting equations (I-27) and (I-29) into equation (I-26) and collecting terms

$$\left(\frac{y_1 - x_1}{1 - y_1}\right) \left(\frac{\partial \mu_1^V}{\partial y_1}\right)_{P,T} dy_1 = (x_1 \Delta \bar{V}_1 + x_2 \Delta \bar{V}_2) dP - (x_1 \Delta \bar{S}_1 + x_2 \Delta \bar{S}_2) dT \quad (I-30)$$

An expression will now be derived for $\left(\frac{\partial \mu_1^V}{\partial y_1}\right)_{P,T}$. By definition of the fugacity f at constant T

$$d\bar{G} = RT d \ln f \quad (dT = 0) \quad (I-31)$$

Therefore

$$d\mu_i^V = RT d \ln \bar{f}_i^V \quad (dT = 0) \quad (I-32)$$

and

$$\mu_i^V = RT \ln \bar{f}_i^V + \mu_i^{\circ V} \quad (I-33)$$

from which

$$\left(\frac{\partial \mu_i^V}{\partial P}\right)_T = RT \left(\frac{\partial \ln \bar{f}_i^V}{\partial P}\right)_T \quad (I-34)$$

From equation (I-11)

$$\left(\frac{\partial \mu_i^V}{\partial P}\right)_{T,n_j} = \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial P}\right)_{T,n_j}\right]_{T,P} = \left(\frac{\partial V}{\partial n_i}\right)_{T,P} = \bar{V}_i \quad (I-35)$$

Substituting equation (I-35) into equation (I-34)

$$\left(\frac{\partial \ln \bar{f}_i^V}{\partial P} \right)_T = \frac{\bar{V}_i}{RT} \quad (\text{I-36})$$

Integrating

$$\ln \frac{\bar{f}_{i2}^V}{\bar{f}_{i1}^V} = \frac{1}{RT} \int_{P_1}^{P_2} \bar{V}_i dP \quad (T \text{ constant}) \quad (\text{I-37})$$

If state 1 is chosen such that $\bar{f}_i = P y_i$, then

$$\ln \frac{\bar{f}_{i2}^V}{P_1 y_i} = \frac{1}{RT} \int_{P_1}^{P_2} \bar{V}_i dP = \frac{1}{RT} \int_{P_1}^{P_2} \left(\frac{RT}{P} - \bar{\alpha}_i \right) dP \quad (\text{I-38})$$

$$\text{where } \bar{\alpha}_i = \frac{RT}{P} - \bar{V}_i \quad (\text{I-39})$$

Expanding and rearranging equation (I-36)

$$RT \ln \bar{f}_{i2} - RT \ln P_1 - RT \ln y_i = RT \ln P_2 - RT \ln P_1 - \int_{P_1}^{P_2} \bar{\alpha}_i dP \quad (\text{I-40})$$

or

$$RT \ln \frac{\bar{f}_{i2}^V}{P_2 y_i} = - \int_{P_1}^{P_2} \bar{\alpha}_i dP \quad (\text{I-41})$$

Letting $P_1 \rightarrow 0$ and $P_2 \rightarrow P$

$$RT \ln \frac{\bar{f}_i^V}{P y_i} = - \int_0^P \bar{\alpha}_i dP = - \int_0^P \left(\frac{RT}{P} - \bar{V}_i \right) dP \quad (\text{I-42})$$

from which

$$RT \ln \bar{f}_i^V = RT \ln y_i + \int_0^P \bar{V}_i dP \quad (\text{I-43})$$

Substituting equation (I-43) into equation (I-33)

$$\mu_i^V = RT \ln y_i + \int_0^P \bar{V}_i dP + \mu_i^{\circ V} \quad (\text{I-44})$$

Differentiating

$$\left(\frac{\partial \mu_i^V}{\partial y_i} \right)_{P,T} = \frac{RT}{y_i} + \int_0^P \left(\frac{\partial \bar{V}_i}{\partial y_i} \right)_{P,T} dP \quad (\text{I-45})$$

If we let

$$\xi_i = \frac{1}{RT} \int_0^P \left(\frac{\partial \bar{V}_i}{\partial y_i} \right)_{P,T} dP \quad (\text{I-46})$$

then

$$y_i \left(\frac{\partial \mu_i^V}{\partial y_i} \right)_{P,T} = RT (1 + y_i \xi_i) \quad (\text{I-47})$$

The equilibrium distribution ratios (K-values) will now be incorporated. From the definition of K-value

$$K_i = \frac{y_i}{x_i} \quad (\text{I-48})$$

it follows that

$$\ln K_1 = \ln y_1 - \ln x_1 \quad (\text{I-49})$$

Differentiating and multiplying both sides by x_1

$$x_1 d \ln K_1 = \frac{x_1 d y_1}{y_1} - dx_1 \quad (\text{I-50})$$

Similarly for the other component

$$x_2 d \ln K_2 = \frac{x_2 d y_2}{y_2} - dx_2 \quad (\text{I-51})$$

Adding equations (I-50) and (I-51)

$$x_1 d \ln K_1 + x_2 d \ln K_2 = \frac{x_1 d y_1}{y_1} + \frac{x_2 d y_2}{y_2} \quad (\text{I-52})$$

$$= \left(- \frac{y_1 - x_1}{1 - y_1} \right) \left(\frac{dy_1}{y_1} \right) \quad (\text{I-53})$$

The chemical potential and K-value expressions will now be incorporated into the equilibrium equation. Substituting equations (I-53) and (I-47) into equation (I-30)

$$x_1 d \ln K_1 + x_2 d \ln K_2 = \frac{(x_1 \Delta \bar{S}_1 + x_2 \Delta \bar{S}_2) dT - (x_1 \Delta \bar{V}_1 + x_2 \Delta \bar{V}_2) dP}{RT(1 + y_1 \xi_1)} \quad (\text{I-54})$$

Restricting equation (I-54) to an isothermal path,

$$x_1 \left(\frac{\partial \ln K_1}{\partial P} \right)_T + x_2 \left(\frac{\partial \ln K_2}{\partial P} \right)_T = - \frac{x_1 \Delta \bar{V}_1 + x_2 \Delta \bar{V}_2}{RT(1 + y_1 \xi_1)} \quad (I-55)$$

$$= \frac{\bar{V}^L - x_1 \bar{V}_1^V - x_2 \bar{V}_2^V}{RT(1 + y_1 \xi_1)} \quad (I-56)$$

Every term can be multiplied by the pressure and the equation can then be expressed in compressibility factors rather than volumes.

$$Z^L = \frac{P \bar{V}^L}{RT}, \quad Z_1^V = \frac{P \bar{V}_1^V}{RT}, \quad \text{and} \quad Z_2^V = \frac{P \bar{V}_2^V}{RT}$$

Recalling that $\frac{P}{dP} = \frac{1}{d \ln P}$

$$x_1 \left(\frac{\partial \ln K_1}{\partial \ln P} \right)_T + x_2 \left(\frac{\partial \ln K_2}{\partial \ln P} \right)_T = \frac{Z^L - x_1 Z_1^V - x_2 Z_2^V}{(1 + y_1 \xi_1)} \quad (I-57)$$

The numerator of the right side can be expressed in values of y_1 , K_1 , and K_2 rather than liquid compositions.

$$Z^L - x_1 Z_1^V - x_2 Z_2^V = Z^L - \left(\frac{y_1}{K_1} \right) Z_1^V - \left(\frac{y_2}{K_2} \right) Z_2^V \quad (I-58)$$

Substituting $\frac{Z^V - \bar{Z}_1^V y_1}{y_2}$ for Z_2^V

$$Z^L - x_1 Z_1^V - x_2 Z_2^V = Z^L - \left(\frac{y_1}{K_1} \right) Z_1^V - \left(\frac{y_2}{K_2} \right) \left(\frac{Z^V - \bar{Z}_1^V y_1}{y_2} \right) \quad (I-59)$$

$$= Z^L - y_1 \bar{Z}_1^V \left(\frac{1}{K_1} - \frac{1}{K_2} \right) - \frac{Z^V}{K_2} \quad (I-60)$$

Using this expression, equation (I-57) becomes

$$x_1 \left(\frac{\partial \ln K_1}{\partial \ln P} \right)_T + x_2 \left(\frac{\partial \ln K_2}{\partial \ln P} \right)_T = \frac{Z_{\text{Mix}}^L - y_1 \bar{Z}_1^V (1/K_1 - 1/K_2) - Z_{\text{Mix}}^V / K_2}{(1 + y_1 \xi_1)} \quad (\text{I-61})$$

Equation (I-61) can also be expressed in integral form, as used by Thompson and Edmister (14)

$$\begin{aligned} & \int_{\ln K_1, P_1}^{\ln K_1, P_2} x_1 (1 + y_1 \xi_1) d \ln K_1 + \int_{\ln K_2, P_1}^{\ln K_2, P_2} x_2 (1 + y_1 \xi_1) d \ln K_2 \\ &= \int_{P_1}^{P_2} \left[Z_{\text{Mix}}^L + y_1 \bar{Z}_1^V (1/K_2 - 1/K_1) - Z_{\text{Mix}}^V / K_2 \right] d \ln P \quad (\text{I-62}) \end{aligned}$$

If the Lewis and Randall rule holds for the vapor, $\xi_1 = 0$ and equation (I-62) reduces to that derived by Adler, et al.

Equation I-56 can be expressed in integral form

$$\int_{\ln K_1, P_1}^{\ln K_1, P_2} x_1 (1 + y_1 \xi_1) d \ln K_1 + \int_{\ln K_2, P_1}^{\ln K_2, P_2} x_2 (1 + y_1 \xi_1) d \ln K_2 = \int_{P_1}^{P_2} \frac{V_{\text{Mix}}^L - x_1 \bar{V}_1^V - x_2 \bar{V}_2^V}{RT} d \ln P \quad (\text{I-63})$$

Equation I-63 is the version actually used in this consistency test.

APPENDIX II

VIRIAL EXPRESSION FOR ξ_1

Thompson (15) has derived an expression for ξ_1 using the Berlin form virial equation. Following is Thompson's derivation

$$\underline{V} = \frac{RT}{P} + B' + C'P \quad (\text{II-1})$$

and

$$V = (n_1+n_2)\underline{V} = \frac{(n_1+n_2)RT}{P} + (n_1+n_2)B' + (n_1+n_2)C'P \quad (\text{II-2})$$

The Berlin form second and third virial coefficients are expressed in Leyden form equivalents because of their preponderance in the literature

$$B' = B = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \quad (\text{II-3})$$

$$= \frac{n_1^2}{(n_1+n_2)^2} B_{11} + \frac{2n_1 n_2}{(n_1+n_2)^2} B_{12} + \frac{n_2^2}{(n_1+n_2)^2} B_{22} \quad (\text{II-4})$$

$$\begin{aligned} C' = \frac{C-B^2}{RT} = \frac{1}{RT} & \left[\frac{n_1^3}{(n_1+n_2)^3} C_{111} + \frac{3n_1^2 n_2}{(n_1+n_2)^3} C_{112} + \frac{3n_1 n_2^2}{(n_1+n_2)^3} C_{122} \right. \\ & + \left. \frac{n_2^3}{(n_1+n_2)^3} C_{222} \right] - \frac{1}{RT} \left[\frac{n_1^4}{(n_1+n_2)^4} B_{11}^2 + \frac{4n_1^2 n_2^2}{(n_1+n_2)^4} B_{12}^2 \right. \\ & + \frac{n_2^4}{(n_1+n_2)^4} B_{22}^2 + \frac{4n_1^3 n_2}{(n_1+n_2)^4} B_{11} B_{12} + \frac{2n_1^2 n_2^2}{(n_1+n_2)^4} B_{11} B_{22} + \left(\frac{4n_1 n_2^3}{(n_1+n_2)^4} \right) \\ & \left. (B_{12} B_{22}) \right] \quad (\text{II-5}) \end{aligned}$$

Substituting equations (II-4) and (II-5) into equation (II-2)

$$\begin{aligned}
 V = & \frac{(n_1+n_2)RT}{P} + \left[\frac{n_1^2}{n_1+n_2} B_{11} + \frac{2n_1n_2}{n_1+n_2} B_{12} + \frac{n_2^2}{n_1+n_2} B_{22} \right] \\
 & + \frac{P}{RT} \left[\frac{n_1^3}{(n_1+n_2)^2} C_{111} + \frac{3n_1^2n_2}{(n_1+n_2)^2} C_{112} + \frac{3n_1n_2^2}{(n_1+n_2)^2} C_{122} \right. \\
 & \left. + \frac{n_2^3}{(n_1+n_2)^2} C_{222} \right] - \frac{P}{RT} \left[\frac{n_1^4}{(n_1+n_2)^3} B_{11}^2 + \frac{4n_1^2n_2^2}{(n_1+n_2)^3} B_{12}^2 + \frac{n_2^4}{(n_1+n_2)^3} B_{22}^2 \right. \\
 & \left. + \frac{4n_1^3n_2}{(n_1+n_2)^3} B_{11}B_{12} + \frac{2n_1^2n_2^2}{(n_1+n_2)^3} B_{11}B_{22} + \frac{4n_1n_2^3}{(n_1+n_2)^3} B_{12}B_{22} \right] \quad (\text{II-6})
 \end{aligned}$$

The definition of \bar{v}_1 , equation 2, contains the partial molal volume

$$\begin{aligned}
 \bar{v}_1 = & \left(\frac{\partial V}{\partial n_1} \right)_{P,T,n_2} = \frac{RT}{P} + \left[\frac{n_1^2+2n_1n_2}{(n_1+n_2)^2} B_{11} + \frac{2n_2^2}{(n_1+n_2)^2} B_{12} - \frac{n_2^2}{(n_1+n_2)^2} B_{22} \right] \\
 & + \frac{P}{RT} \left[\frac{(n_1^3+3n_1^2n_2)}{(n_1+n_2)^3} C_{111} + \frac{6n_1n_2^2}{(n_1+n_2)^3} C_{112} + \frac{(3n_1^3-3n_1n_2^2)}{(n_1+n_2)^3} C_{122} \right. \\
 & \left. - \frac{2n_2^3}{(n_1+n_2)^3} C_{222} \right] - \frac{P}{RT} \left[\frac{(n_1^4+4n_1^3n_2)}{(n_1+n_2)^4} B_{11}^2 + \frac{(8n_1n_2^3-4n_1^2n_2^2)}{(n_1+n_2)^4} B_{12}^2 \right. \\
 & \left. - \frac{3n_2^4}{(n_1+n_2)^4} B_{22}^2 + \frac{12n_1^2n_2^2}{(n_1+n_2)^4} B_{11}B_{12} + \frac{4n_1n_2^3-2n_1^2n_2^2}{(n_1+n_2)^4} B_{11}B_{22} \right. \\
 & \left. + \frac{4n_2^4-8n_1n_2^3}{(n_1+n_2)^4} B_{12}B_{22} \right] \quad (\text{II-7})
 \end{aligned}$$

Dividing by RT , subtracting $1/P$, and expressing the coefficients in mol fractions

$$\begin{aligned}
 \frac{\bar{V}_1}{RT} - \frac{1}{P} = & \frac{1}{RT} \left[(y_1^2 + 2y_1y_2)B_{11} + 2y_2^2B_{12} - y_2^2B_{22} \right] + \frac{P}{R^2T^2} \left[(y_1^3 + 3y_1^2y_2)C_{111} \right. \\
 & + 6y_1y_2^2C_{112} + (3y_2^3 - 3y_1y_2^2)C_{122} - 2y_2^3C_{222} \left. \right] - \frac{P}{R^2T^2} \left[y_1^4 + 4y_1^3y_2 \right. \\
 & + (8y_1y_2^3 - 4y_1^2y_2^2)B_{12}^2 - 3y_2^4B_{22}^2 + 12y_1^2y_2^2B_{11}B_{12} + (4y_1y_2^3 - 2y_1^2y_2^2) \\
 & \left. (B_{11}B_{12}) + (4y_2^4 - 8y_1y_2^3)B_{12}B_{22} \right] \quad (II-8)
 \end{aligned}$$

Integrating and expressing concentration in y_1 exclusively

$$\begin{aligned}
 \int_0^P \left(\frac{\bar{V}_1}{RT} - \frac{1}{P} \right) dP' = & \frac{P}{RT} \left[(2y_1 - y_1^2)B_{11} + (2 - 4y_1 + 2y_1^2)B_{12} - (1 - 2y_1 + y_1^2)B_{22} \right. \\
 & + \frac{P^2}{2R^2T^2} \left[(3y_1^2 - 2y_1^3)C_{111} + (6y_1 - 12y_1^2 + 6y_1^3)C_{112} + (3 - 12y_1 + 15y_1^2 \right. \\
 & - 6y_1^3)C_{122} - (2 - 6y_1 + 6y_1^2 - 2y_1^3)C_{222} \left. \right] - \frac{P^2}{2R^2T^2} \left[(4y_1^3 - 3y_1^4)B_{11}^2 \right. \\
 & + (8y_1 - 28y_1^2 + 33y_1^3 - 12y_1^4)B_{12}^2 - (3 - 12y_1 + 18y_1^2 - 12y_1^3 + 3y_1^4)B_{22}^2 \\
 & + (12y_1^2 - 24y_1^3 + 12y_1^4)B_{11}B_{12} + (4y_1 - 14y_1^2 + 16y_1^3 - 6y_1^4)B_{11}B_{12} \\
 & \left. + (4 - 24y_1 + 48y_1^2 - 40y_1^3 + 12y_1^4)B_{12}B_{22} \right] \quad (II-9)
 \end{aligned}$$

Equation 2, the definition of ξ_1 , can be written

$$\xi_1 = \frac{\partial}{\partial y_1} \left[\int_0^P \left(\frac{\bar{V}_1}{RT} - \frac{1}{P} \right) dP' \right] \quad (II-10)$$

Performing the indicated differentiation and expressing concentration in y_2 where convenient

$$\begin{aligned}\xi_1 = & \frac{P}{RT} \left[2y_2 B_{11} - 4y_2 B_{12} + 2y_2 B_{22} \right] + \frac{P^2}{2R^2 T^2} \left[6y_1 y_2 C_{111} + 6y_2 (y_2 - 2y_1) C_{112} \right. \\ & - 6y_2 (2y_2 - y_1) C_{122} + 6y_2^2 C_{222} \left. \right] - \frac{P^2}{2R^2 T^2} \left[12y_1^2 y_2 B_{11}^2 + 8y_2^2 (1 - 6y_1 y_2) B_{12}^2 \right. \\ & + 12y_2^3 B_{22}^2 + 24y_1 y_2 (y_2 - y_1) B_{11} B_{12} + 4y_2 (1 - 6y_1 y_2) B_{11} B_{22} \\ & \left. - 24y_2^2 (y_2 - y_1) B_{12} B_{22} \right] \quad (II-11)\end{aligned}$$

$$\begin{aligned}\xi_1 = & \frac{2Py_2}{RT} \left[B_{11} + B_{22} - 2B_{12} \right] + \frac{3P^2 y_2}{R^2 T^2} \left[y_1 C_{111} + (y_2 - 2y_1) C_{112} + (y_1 - 2y_2) C_{122} \right. \\ & \left. + y_2 C_{222} \right] - \frac{2P^2 y_2}{R^2 T^2} \left[3y_1^2 B_{11}^2 + 3y_2^2 B_{22}^2 + (1 - 6y_1 y_2) (B_{11} B_{22} + 2B_{12}^2) \right. \\ & \left. + 6(y_2 - y_1) (y_1 B_{11} B_{12} - y_2 B_{12} B_{22}) \right] \quad (II-12)\end{aligned}$$

$$\begin{aligned}\xi_1 = & \frac{2Py_2}{RT} \left(\left[B_{11} + B_{22} - 2B_{12} \right] + \frac{3P}{2RT} \left[y_1 C_{111} + (y_2 - 2y_1) C_{112} \right. \right. \\ & \left. + (y_1 - 2y_2) C_{122} + y_2 C_{222} \right] - \frac{P}{RT} \left[3(y_1^2 B_{11}^2 + y_2^2 B_{22}^2) \right. \\ & \left. \left. + (1 - 6y_1 y_2) (B_{11} B_{22} + 2B_{12}^2) + 6B_{12} (y_2 - y_1) (y_1 B_{11} - y_2 B_{22}) \right] \right) \quad (II-13)\end{aligned}$$

Attempts to derive an expression for ξ_1 , from the Leiden form virial equation of state were unsuccessful, as were attempts to derive an expression from the Redlich-Kwong equation.

APPENDIX III

The Redlich-Kwong (10) equation of state is

$$P = \frac{RT}{V-b} - \frac{a}{T^{0.5} V(V+b)} \quad (\text{III-1})$$

It also takes the form

$$Z = \frac{1}{1-h} - \frac{A^2}{B} \left(\frac{h}{1+h} \right) \quad (\text{III-2})$$

where

$$A^2 = \frac{a}{R^2 T^{2.5}} = 0.4278 T_c^{2.5} / P_c T^{2.5} \quad (\text{III-3})$$

$$B = \frac{b}{RT} = \frac{0.0867 T_c}{P_c T} \quad (\text{III-4})$$

$$h = \frac{BP}{Z} = \frac{b}{V} \quad (\text{III-5})$$

Equation (III-2) was programmed for the computer. This program solves for Z by an iteration scheme involving interval halving. This program used the mixing rules suggested by Redlich and Kwong, i.e.

$$b = \sum_j y_j b_j \quad (\text{III-6})$$

$$B = \sum_j y_j B_j \quad (\text{III-7})$$

$$a = a_1 y_1^2 + a_2 y_2^2 + \dots + 2a_{12} y_1 y_2 + \dots \quad (\text{III-8})$$

$$a_{12} = (a_1 a_2)^{1/2} \quad (\text{III-9})$$

$$A = \sum_j y_j A_j \quad (\text{III-10})$$

The Prausnitz (9) equation for \bar{V}_1^V is based on the relationship

$$\bar{V}_1 = \frac{-(\partial P / \partial n_1)_{T,V,n_2}}{(\partial P / \partial V)_{T,n_1,n_2}} \quad (\text{III-11})$$

The corresponding equation, which he derived from the Redlich-Kwong is

$$\bar{V}_1 = \frac{\left[T^{1/2} V(V+b) \right]^{-1} \left\{ 2y_1 a_1 + 2y_2 \sqrt{a_1 a_2} - \left[a b_1 / (V+b) \right] \right\} - \left[RT / (V-b) \right] \left\{ 1 + \left[b_1 / (V-b) \right] \right\}}{\left(a / T^{1/2} \right) \left[(2V+b) / V^2 (V+b)^2 \right] - \left[RT / (V-b)^2 \right]} \quad (\text{III-12})$$

The Strobridge (13) equation for the density of saturated liquid nitrogen is

$$\rho = k_1 + k_2 x + k_3 x^2 + k_4 x^3 + k_5 x^4 \quad (\text{III-13})$$

where

$$x = \left[1 - \frac{T}{126.26} \right]^{1/3} \quad (\text{III-14})$$

The constants k_1 through k_5 have numerical values given by Strobridge.

APPENDIX IV

At the beginning of this test, most isotherms had equations as high as the fifth degree fitted to them and some went as high as the thirteenth degree. These higher degree equations frequently gave better apparent fits to the curve (i.e., smaller residuals). However, integration of these equations produced impossible results.

For the right side of the equation for one isotherm twelve different polynomial curves were fitted. They were of the type

$$\begin{aligned} \underline{V}^L - x_1 \bar{V}_1 - x_2 \bar{V}_2 &= A + \frac{B}{P} + \frac{C}{P^2} \\ &= A' + \frac{B'}{P} + \frac{C'}{P^2} + \frac{D'}{P^3} \\ \text{etc., up to} &= A'' + \frac{B''}{P} + \frac{C''}{P^2} + \frac{D''}{P^3} \dots \frac{M''}{P^{13}} \end{aligned}$$

Table IV-1 lists the degree of each of these polynomials, the standard estimate of error for each one (based on how well the curve fits the data), and the area under each of the integrated polynomials.

TABLE IV-1 - Integration of various polynomials

| Degree of Polynomial | Standard Estimate of Error | Area Under Integrated Polynomial |
|----------------------|-------------------------------|-------------------------------------|
| 2 | .000702 | -4.00 |
| 3 | .000474 | -4.02 |
| 4 | .000269 | -3.68 |
| 5 | .0000875 | -11.05 |
| 6 | .0000922 | 6.77 |
| 7 | .0000164 | -15,844 |
| 8 | .0000178 | 187,360 |
| 9 | .0000197 | -1,231,247 |
| 10 | .0000219 | 1,252,326 |
| 11 | .0000252 | 1,466,312 |
| 12 | .0000311 | 1,686,911 |
| 13 | .0000384 | 7,247,713 |

The first two answers were in good agreement. The next was poor, and the rest absurd. It developed that the higher degree equations were producing "tear drops" between the actual points. This is illustrated in figure IV-1.

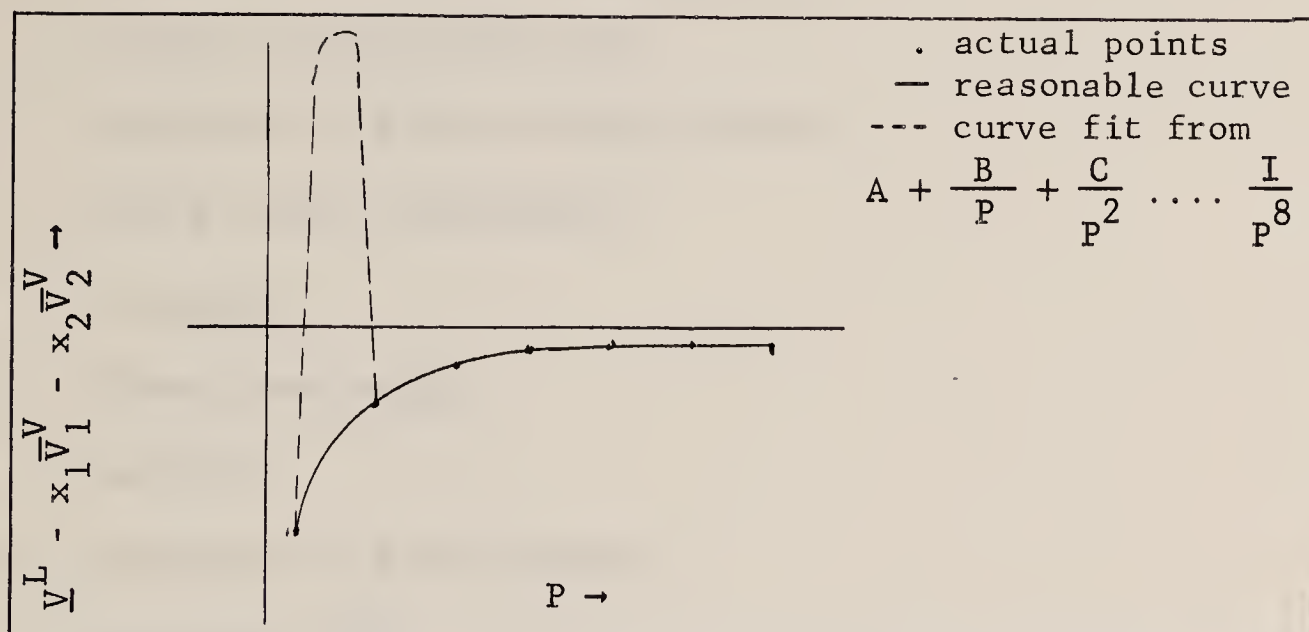


Figure IV-1. - "Tear drop" from higher degree equation for A_3

The two lower degree equations produced no such "tear drops."

Thereafter, only second, third, and fourth degree equations were fitted for A_1 and A_2 . For A_3 equations of the first, second, and third degree in the reciprocal of P were generated.

NOMENCLATURE

- A = parameter of Redlich-Kwong equation
 = area of an integral
 a = parameter of Redlich-Kwong equation
 B = parameter of Redlich-Kwong equation
 = second virial coefficient
 b = parameter of Redlich-Kwong equation
 C = third virial coefficient
 f = fugacity
 G = Gibbs free energy
 H = enthalpy
 h = parameter of Redlich-Kwong
 equation = $\frac{BP}{Z}$
 K = vapor-liquid equilibria phase
 distribution ratio, y/x
 = Kelvin temperature
 k = constant in Strohbridge equation
 n = number of moles
 = number of components
 P = pressure
 R = universal gas constant
 S = entropy
 T = temperature
 U = internal energy
 V = volume

x = liquid-phase composition

y = vapor-phase composition in equilibrium with x

Z = compressibility factor, PV/RT

Greek Letters

α = $RT/P - V$

Δ = change in a quantity

μ = chemical potential

ρ = density in gram moles/liter

$$\xi = \frac{1}{RT} \int_0^P \left(\frac{\partial \bar{v}_i}{\partial y_i} \right)_{P,T} dP$$

Subscripts

c = critical property

i = i^{th} component

j = j^{th} component

Mix = mixture

1 = lighter component

= first integral of consistency test

= lower limit of integration

2 = heavier component

= second integral of consistency test

= lower limit of integration

3 = third integral of consistency test

1-5 = different constants in Strohbridge equation

subbar = molal quantity

Superscripts

L = liquid state

V = vapor state

° = ideal state

' = Berlin form

superbar = partial molal quantity

Abbreviations

ln = logarithm to the base e

PVT = pressure-volume-temperature

R-K = Redlich-Kwong

